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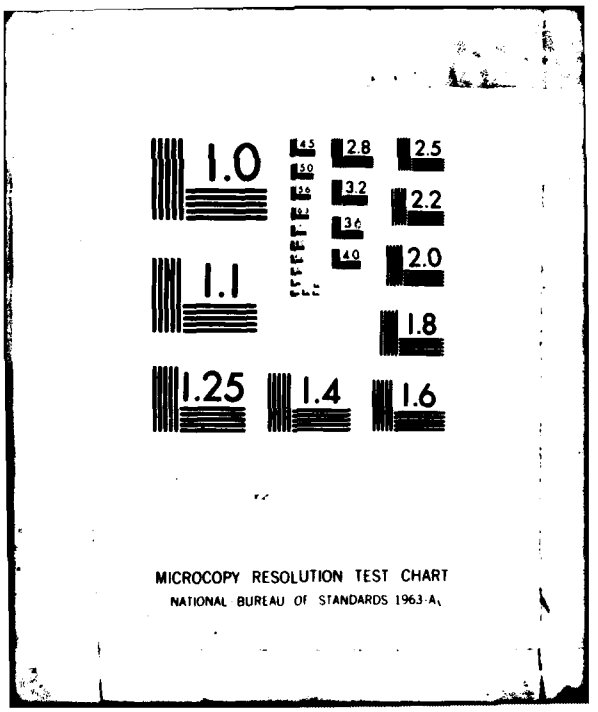
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The theoretically predicted shift of vibronic components and change of their distribution under high pressure were confirmed by the low temperature emission spectra of the natural crystal scapolite.

The insensibility of the self-activated luminescence in the ZnS : B crystals to the high pressure action indicated that it comes from a tightly associated new luminescence center. .../

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20. Abstract (continued)

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RESEARCH ON THE EFFECTS OF HYDROSTATIC PRESSURE ON THE ELECTRONIC STATES OF IMPURITIES

Final technical report

by

Professor J. MATTLER

European Research Office
United States Army
London, England

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Laboratoire de Luminescence
Université P. et M. Curie
Tour 13 - 5° étage
4, place Jussieu
75230 Paris Cedex 05, France

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Abstract

The theoretically predicted shift of vibronic components and change of their distribution under high pressure were confirmed by the low temperature emission spectra of the natural crystal scapolite.

The insensibility of the self-activated luminescence in the ZnS : B crystals to the high pressure action indicated that it comes from a tightly associated new luminescence center.

The differences between the high pressure action on the cubic and hexagonal ZnS : Mn crystals are interpreted by the resonance energy transfer.

The pressure shifts of the excitonic excitation bands in the ZnS and ZnSe crystals agree with the gap shifts calculated for these crystals but are smaller than the experimentally found pressure shifts of the donor-acceptor luminescence bands.

RESEARCH ON THE EFFECTS OF HYDROSTATIC PRESSURE ON THE ELECTRONIC STATES OF IMPURITIES

The high pressure (H. P.) optical spectra of the II-VI crystals as well as of a natural crystal of scapolite have been studied.

A. EMISSION SPECTRA

A, 1 - The luminescence spectrum of the scapolite crystal [a rock-forming mineral solid solution with the general formula : $(Na, Ca)_4$ $(Al, Si)_{12}$ O_{24} (Cl, CO_3, SO_4)] gave us the possibility to check the fundamental theory of the HP-action on the electronic levels involved in the radiative transition.

The luminescence of this crystal comes from the molecular centers S_2^- and exhibits a pronounced vibronic structure (fig. 1). It enables us therefore to study the HP action on the individual vibronic components and to observe two pressure effects predicted by the theory : a) a change in the transition energies of individual vibronic lines and, b) a change of their relative intensities [1] [2] .

In most luminescent materials with a large Huang and Rhys parameter, the vibronic structure is not well resolved and only changes in the envelope spectra can be observed. The spectra of scapolite luminescence excited with the 4 100 Å radiation at 70 K were taken under normal pressure and at $\sim$ 6 kbars.

One sees (fig. 1) that pressure shifts the vibronic bands towards higher energies. This shift decreases while the number n of the vibronic band increases : so it is equal to 1, 23 meV/kbar for n = 3 and to 0. 61 meV/kbar for n = 10.

On the other hand the intensity of the higher energy bands becomes relatively stronger under pressure, thus contributing to the blue shift of the envelope emission, which appears to be 2.5 - 3 times more important than the shift of the individual bands. These results correspond to the pressure action predicted by the theory.

The study of the luminescence in ZnS crystals under pressure was devoted to some particular problems : first we elucidated the nature of a new luminescent center in ZnS : B (A. 2) and then we studied the mechanism of energy transfer in ZnS : Mn (A. 3).

A. 2 - We observed a peculiar self-activated luminescence in ZnS crystals containing boron (B) : the emission band is narrower than in ZnS : Cl and ZnS : Al, its half-width is 0.23 eV at 4.2 K and increases with the temperature, following exactly the configurational coordinate model predictions. The intensity of this luminescence decreases rapidly upon heating above 77 K. The blue luminescence ZnS : B is excited strongly at 4.2 K, in contradistinction to the donor-acceptor pair (D-A) emission in ZnS : Cl, by the excitons close to gap. No photosensitive electron spin resonance (EPR) signals follow the excitation of luminescence in ZnS : B.

All these results had led us to the assumption, that the luminescence in ZnS : B is due to the localized transition occuring in the complex system constituted by a substitutional B_{Zn} atom tightly associated to a zinc vacancy V_{Zn}.

This assumption was borne out by the pressure results : whereas the self-activated (S-A) emission band in ZnS : Cl shifts strongly under pressure towards higher energies, as do the other D-A pair luminescence bands [for cubic ZnS : Cl $dE/dP = (10.4 \pm 0.6)$ meV/kbar] , there is no measurable shift of the emission in ZnS : B with pressure : $dE/dP = (0.0 \pm 0.6)$ meV/kbar [3].

A. 3 - The orange luminescence of the ZnS : Mn crystals under

365 nm excitation at 300 K comes from the energy transfer between the blue emitting S-A and orange emitting Mn^{2+} centers. This transfer had been ascribed to the thermal deexcitation of the S-A centers and subsequent excitation of the Mn^{2+} centers by the recombining free charges. However, we observed a difference in the pressure action on the luminescence spectrum of the cubic and hexagonal ZnS : Mn crystals, this indicating clearly that in addition to the preceding one a different transfer mechanism should be also taken in account. It appears namely that the relative intensity of the Mn^{2+} emission increases with pressure in the cubic ZnS : Mn crystal and decreases in the hexagonal one. This result could be explained, if one considers the quantum resonance energy transfer from the S-A to the Mn^{2+} centers in these two crystals. The peak of the luminescence S-A band is at 4 780 Å in the cubic and at 4 630 Å in the hexagonal crystal. Pressure shifts strongly this emission band towards higher energies and therefore up to 6 kbars its overlap with the $^4E\ (^4G)\ Mn^{2+}$ absorption band, which peaks at 4 650 Å, increases in the cubic ZnS : Mn and diminishes in the hexagonal ZnS : Mn.

The HP-sensibilization of the Mn^{2+} luminescence appears to follow the overlap of the S-A emission with the $^4E\ (^4G)\ Mn^{2+}$ absorption in both crystals for all applied pressures [4].

B. EXCITATION SPECTRA

The excitation mechanism for the D-A pair luminescencence in the II-VI crystals is not well known. There was not found - in contradistinction to the III-V compounds - a fine spectrum corresponding to the excitation of various pairs. On the other side, the assumption that the excitation of the pairs occurs only via band-band transitions is obviously not sufficient because it does not take in account the observed structure of the excitation spectra.

We understook therefore the study of the pressure action on these

spectra in order to elucidate the nature of the excitation processes. We studied the excitation spectra of the self-activated (S-A) luminescence in ZnS and ZnSe, the donor-acceptor pair mechanism of this luminescence being established by various methods. We observed in these spectra not only the large, well known bands, but also some narrow excitonic bands close to the gap.

One ZnS : Mn, Cl crystal and several ZnSe crystals were excited at R. T. under various pressures from normal to $\sim$ 7 kbars.

A strong excitonic band appears at 3.688 eV in the S-A excitation spectrun of the ZnS : Mn, Cl crystal ; it is accompanied by a weak satellite at 3.746 eV. We ascribe the narrow band to a direct A-exciton and its satellite to the C-exciton (fig. 2).

The pressure coefficient of the A exciton determined from the series of measurements is : $dE/dP = (6.42 \pm 0.10)$ meV/kbar. This value is close to the calculated values of the pressure coefficient for the gap in ZnS, as well as to dE_{gap}/dE determined experimentally by various methods some time ago [5]. The narrow excitation bands in ZnSe peak at 2.681 eV (crystal I), 2.662 eV (crystal II) and 2.672 eV (crystal III and IV).

Excitation spectra in ZnSe were too studied under pressure : at 300 K for the crystals II and III and at different temperatures from 300 K to 80 K for the crystal IV (fig. 3). All these measurements give the same value for the pressure coefficient of the excitonic band : $dE/dP = (7.5 \pm 0.6)$ meV/kbar which again, is close to the calculated value of dE_{gap}/dE for ZnSe [6].

On the other hand, the D-A pair luminescence in these crystals is shifted by pressure stronger than the studied excitons. For instance, we found $dE/dP = 6.9$ meV/kbar for the green luminescence in ZnS : Cu, 7.9 meV/kbar for the red luminescence in ZnS : Fe and 8.5 meV/kbar for the red luminescence in ZnSe : Cu.

The presently available data on the pressure dependence for the

donor-acceptor levels as well as that for the dielectric constant are not sufficient in order to establish a theoretical relationship between the pressure shifts of the gap, of the D-A transitions and of the excitons in the II-VI crystals.

Our measurements showed that the self-activated emission spectrum in ZnS appears to be the same under the excitonic excitation as under the Wood light excitation ; it comes in both cases from the same series of D-A pairs. Obviously, the energy transfer from the excitons to the centers is different in our case than in the experiments of T. Hoshina and H. Kawai [7] who concluded that the excitons may excite only the discrete or tightly associated centers, but not the series of D-A pairs.

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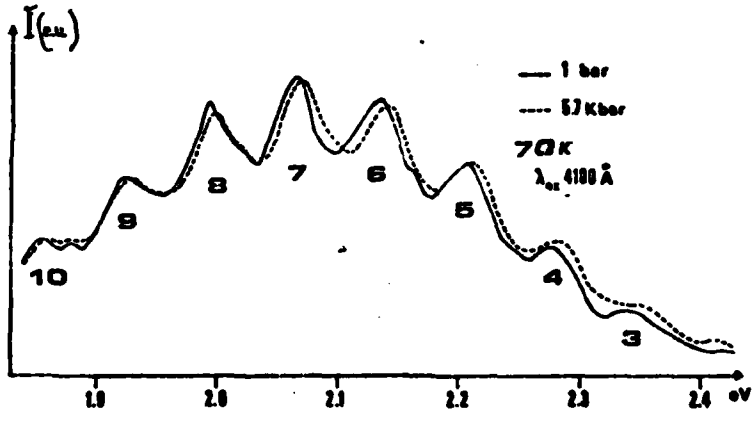

Figure 1 : Scapolite emission spectrum
3, 4, . . = n = vibronic component number

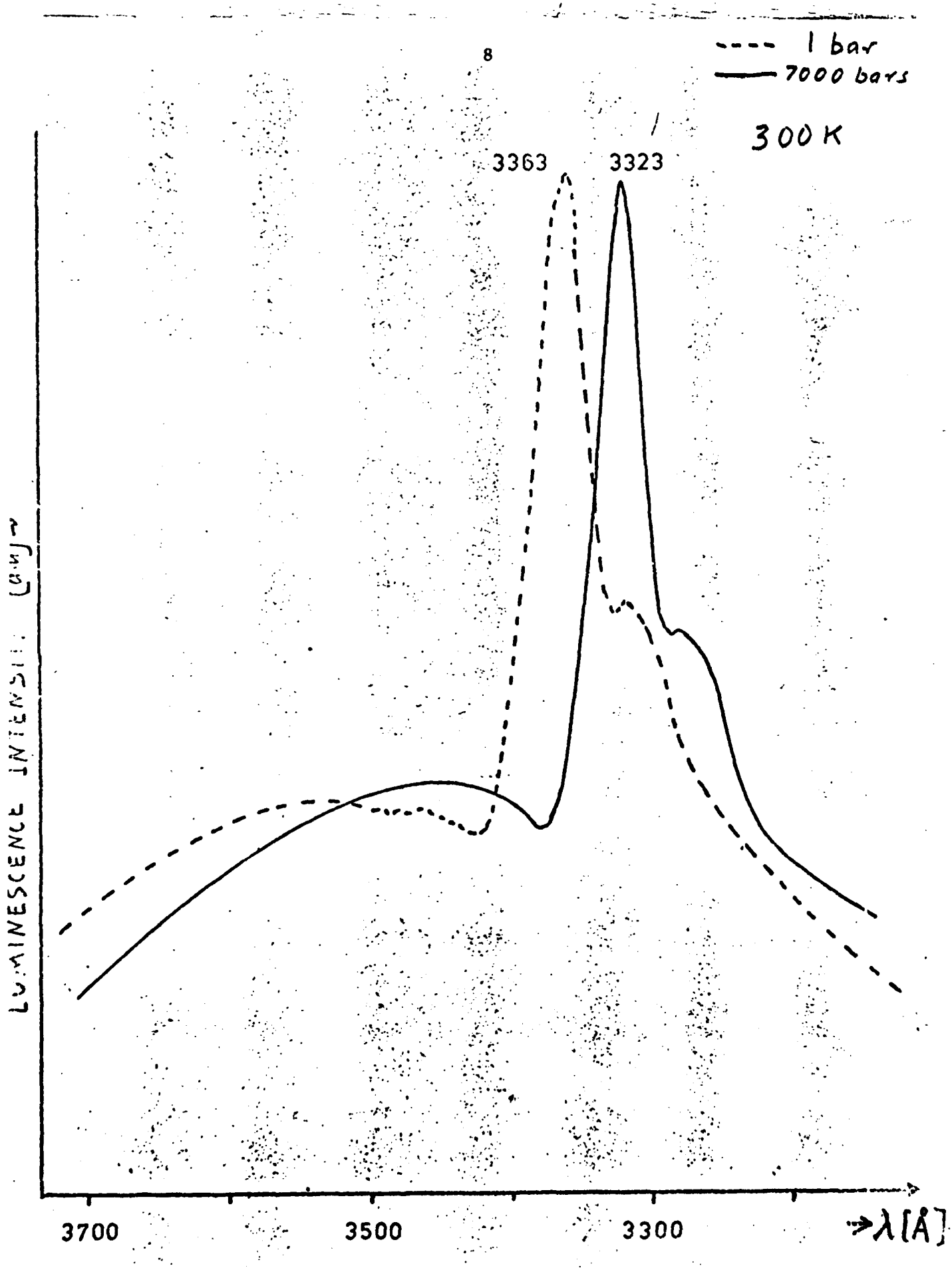

Figure 2 : Registered excitation spectrum for self-activated luminescence in ZnS : Mn, Cl

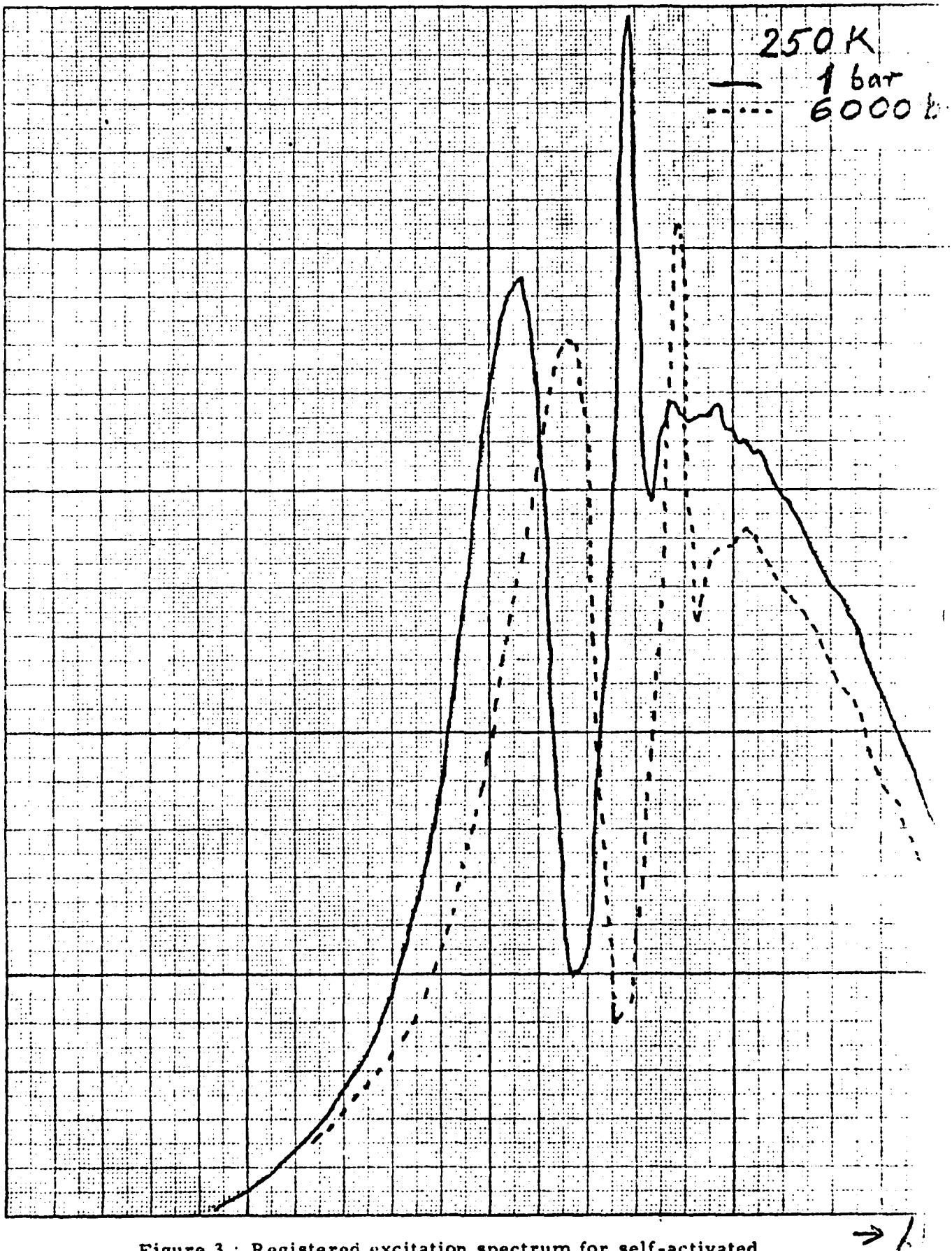

Figure 3 : Registered excitation spectrum for self-activated luminescence in ZnSe.

ABSTRACTS OF APPENDICES

Appendix I The effects of hydrostatic and uniaxial pressures on vibronic spectra

D. Curie, B. Canny, P. Jaszczyn-Kopec, H.K. Liu, D. Berry and F. Williams

Abstract We describe in this paper experimental data and theoretical analyses of broad band spectra and also spectra which show pronounced vibronic structure. Two effects are predicted from the theory : a) a change in the transition energies of individual vibronic lines ; b) a change in the relative intensities of these lines.

In most luminescent materials with large Huang-Rhys parameters, the vibronic structures are not well resolved and only changes in the envelope spectra can be observed. Then a) results in a shift in the same direction for both absorption and emission spectra, while b) results in shifts in opposite directions.

Molecular centers such as O_2^- and S_2^- in alkali halides or in scapolite crystals show detailed vibronic structure even at moderately low temperatures, and both a) and b) effects are clearly observed. The effects of anharmonicity must also be taken into account in interpreting these spectra.

Some attention is also given to the pressure dependence of radiative transitions of donor-acceptor pairs in large gap semiconductors.

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Appendix II The boron center : a new luminescent center in ZnS Crystals

P. Jaszczyn-Kopec, H.D. Fair Jr. and D.S. Downs

Abstract In ZnS crystals containing B, insensitivity of the emission to high pressure, the structure of the excitation spectra and the observed absence of the photo-excited EPR signals suggest that the luminescence may be due to a localized transition between closely associated B_{Zn} and V_{Zn}.

J. of Luminescence 18/19, 837 (1979)

Appendix III High Pressure action on the S-A and Mn emission in the cubic, faulted and hexagonal ZnS crystals

P. Jaszczyn-Kopec, J.P. Pinceaux, M. Zigone, J.M. Kennedy and A. Stadtmuller

Abstract The pressure coefficient dE/dP appears to be sensitive to the ZnS lattice symmetry for the S-A donor-acceptor pair, but not for the Mn^{2+} centers emission.

The HP variation of the relative intensities for the S-A and Mn emissions suggests a resonant transfer between these centers. The classical Dexter's formula for P_{dd} does not explain the results for the cubic crystal, whereas the preferential transfer from the S-A centers to the ^4E (^4G) level in Mn^{2+} follows all reported observations.

Solid State Communications, 32, 473 (1979)

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